

STABILITY CONSTANTS FOR THE CHLORIDE COMPLEXES  
OF PALLADIUM (II)

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# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

STABILITY CONSTANTS FOR THE CHLORIDE  
COMPLEXES OF PALLADIUM (II)

by

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December 1972

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Stability Constants for the Chloride

Complexes of Palladium (II)

by

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Submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

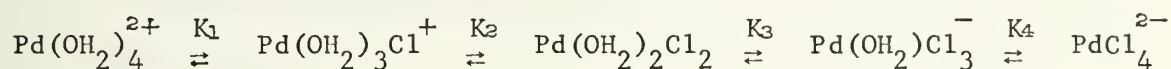
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December 1972



ABSTRACT

Using absorbance data from Pd (II) solutions containing varying amounts of chloride ion, the stepwise formation constants were determined for the following system:



The values for  $K_1$  and  $K_4$  were obtained by curve fitting methods.  $K_2$  and  $K_3$  were found by regression and required statistical adjustment.

Anomalies arising from the resulting values and values obtained by other workers were discussed. Suggestions for further work in the chloro-Pd(II) system were made.





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### ACKNOWLEDGEMENT

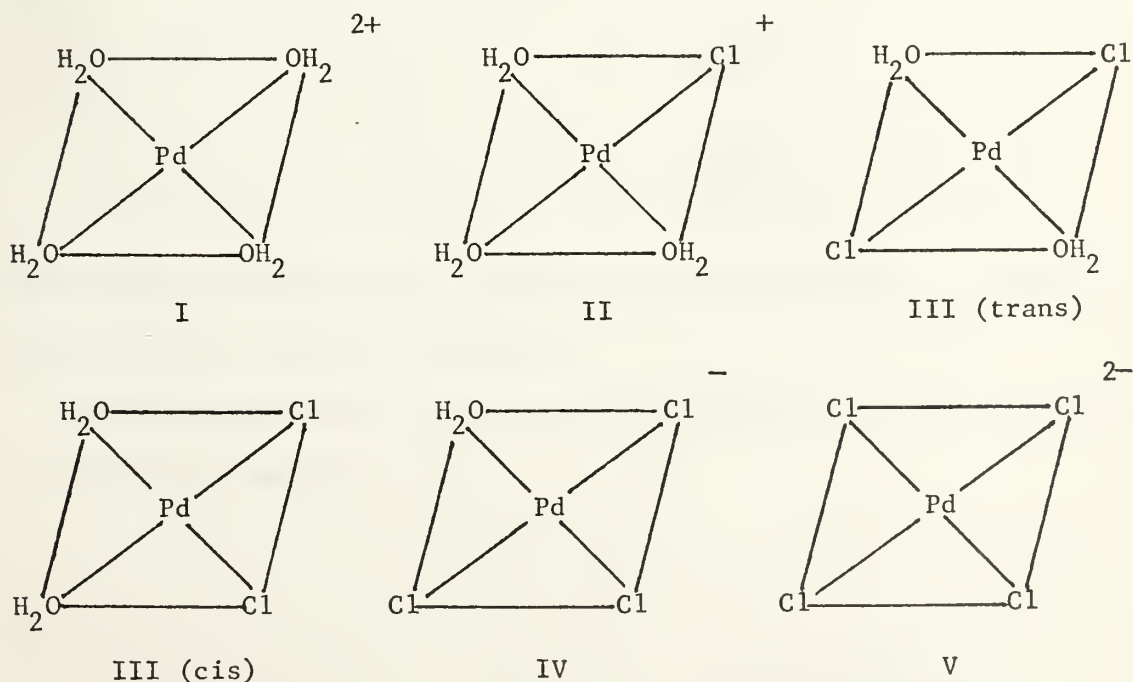
The author wishes to thank Prof. Glenn A. Stoops of the Department of Mathematics for his help with the statistical adjustment of the data; Ken Graham, not only for his typing, but also for his assistance in Hewlett-Packard programming; and Dr. Richard A. Reinhardt for his patience and understanding -- and especially for his guidance. Special appreciation goes to my wife, Suzie, for her loving help and encouragement; and to my sons, Kendal and Brendon, simply for time spent with me.



## I. INTRODUCTION

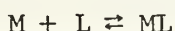
### A. GENERAL

As is the case with nickel (Ni), the +2 state of palladium (Pd) is the more common state, although palladium (IV) is also important [Ref. 1]. Palladium in the +2 state was studied during this research. Along with some of the other platinum group metals {Pt (II), Rh (I), Ir (I)}, Pd (II) has a  $d^8$  electronic configuration and a coordination number of four, such that the complexes formed are square planar [Ref. 2]. These square-planar complexes are formed when a total of four neutral (e.g.,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ) or anionic (e.g.,  $\text{CN}^-$ ,  $\text{CH}_3^-$ , halide) ligands are tightly held to the central metal cation by electron pair sharing, so-called dative or coordinate bonding [Ref. 1]. Square planar is the geometric description of the complex, be it anionic, neutral, or cationic [Ref. 3]. The square-planar complexes studied in this thesis research were:





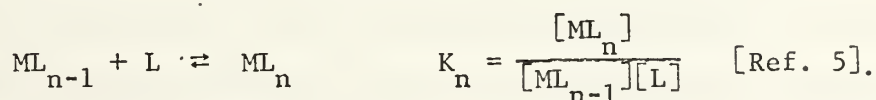
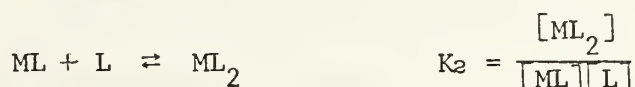
The currently accepted mechanism for substitution of square-planar complexes is believed to be essentially  $S_N2$  with the formation of a trigonal bipyramid intermediate [Ref. 4]. However, of more importance to a study of equilibria in solutions is a distinction between reactivity and stability of complex ions in these solutions. The reactivity of a species refers to the speed with which transformations leading to the attainment of equilibrium will occur. The thermodynamic stability of a species is a measure of the extent to which a species will form from or be transformed into another species under certain conditions when the system has reached equilibrium [Ref. 1]. For example, if M is a transition metal, and L a monodentate ligand, then for the reaction



the thermodynamic equilibrium expression is

$$K_1 = \frac{[ML]}{[M][L]}$$

Similarly, if more ligands are bound to the metal by stepwise formation, then



The subject of this thesis research is the determination of stepwise thermodynamic formation constants.

Another useful way of expressing equilibrium relations is by overall formation constants, e.g.,

$$\beta_1 = K_1$$

$$\beta_2 = K_1 K_2$$

$$\beta_n = K_1 K_2 \dots K_n \quad [\text{Ref. 6}].$$



As will be shown later in the treatment of data and results section, the  $K_i$ 's for this research were determined by first obtaining the  $\beta_i$ 's.

## B. ABSORBANCE

Whether an equilibrium constant is explicitly expressed as a quotient of product and reactant concentrations or as a ratio of the forward and reverse rate constants [Ref. 7], the equilibrium constant remains a mathematical function of concentrations. The task then becomes to measure either the concentrations of the various species present in the system at equilibrium or another property which is linearly dependent on concentration, if the equilibrium constant is to be determined. According to Beer's Law, absorbance of a chemical species in solution is a property which is linearly dependent on concentration [Ref. 8]:

$$A = \epsilon c \ell$$

where,  $A = \log_{10} I/I_0$   
 $\ell$  = optical path length through the sample (cm)  
 $c$  = concentration of the absorbing species (moles/liter)  
 $\epsilon$  = proportionality constant called molar absorptivity when  $\ell$ ,  $c$  and  $A$  are defined as above.

Absorbance is an additive property -- that is to say it applies to a solution containing more than one absorbing species [Ref. 9], such as a solution containing more than one of the square-planar complexes studied in this research. For these reasons, absorbance has long been used as an analytical method and is used in this research in lieu of concentrations for determining equilibrium constants.

## C. CHLORO COMPLEXES OF PALLADIUM (II)

During the time from the mid 1950's to present, a great deal of interest has been generated in the equilibria involving the various chloro complexes of palladium (II). Droll [Ref. 10] reported equilibrium





constants of  $\log K_1 = 6.1$ ,  $\log K_2 = 4.6$ ,  $\log K_3 = 2.4$ , and  $\log K_4 = 2.6$  for successive formation of chloride complexes of Pd (II). Rasmussen and Jørgensen [Ref. 11] argued, however, that these values were high. In addition, Rasmussen and Jørgensen list values reported by Weed [Ref. 12] of 4.4, 3.34, 2.34, and 1.38; by Burger [Ref. 13] of 3.88, 3.06, 2.14, and 1.34; and by Shchukarev et al [Ref. 14] of 4.34, 3.54, 2.61, and 1.68. In light of the differences among the reported values, this research was conducted as a part of a program concerned also with the substitution kinetics in the system.



## II. EXPERIMENTAL

### A. MATERIALS

All materials in this research were reagent grade and were used without further purification.

A stock solution of tetraaquopalladium (II) ion was prepared by dissolving hydrated palladium (II) sulfate ( $\text{PdSO}_4 \cdot x\text{H}_2\text{O}$ ) in 1M  $\text{HClO}_4$  (Baker's analyzed reagent). The  $\text{PdSO}_4$  was prepared by the method of Berzelius (1828) as reported by Mellor [Ref. 15]. Palladous nitrate (Fisher Scientific Company) was boiled in concentrated sulfuric acid (Baker analyzed reagent) for approximately 18 hours, adding  $\text{H}_2\text{SO}_4$  when necessary. The resulting  $\text{PdSO}_4$  was a mixture of the brick-red anhydrous and the brown, partly hydrated forms [Ref. 11]. When placed in 1M  $\text{HClO}_4$ , the brick-red anhydrous form would not dissolve, even after stirring with a magnetic stirrer for several days. The undissolved particles were filtered from the bright yellow solution. An absorbance spectrum was obtained in the visible range (350nm to 550nm) which indicated an absorbance maximum at  $\lambda = 384\text{nm}$ . The shape of the curve and the absorbance maximum agree very closely with that reported for  $\text{Pd}(\text{OH}_2)_4^{2+}$  by Rasmussen and Jørgensen [Ref. 11] and by DeBerry [Ref. 16]. This indicated no inner-sphere sulfate complexes had formed.

A stock solution of tetrachloropalladate ion was prepared by dissolving 7.3545 grams of sodium tetrachloropalladate (Alfa Inorganics) in 500ml of solution using 0.1M  $\text{HCl}$  (CHEMTAM, 1/10 N, from BIO•RAD Laboratories) as solvent. The absorbance spectrum of this solution agreed with the absorbance data for  $\text{PdCl}_4^{2-}$  from Cohen and Davidson [Ref. 17].



All solutions used in determining the equilibrium constants were prepared by dilutions of the stock solutions described above. Chloride ion concentration was varied by the addition of sodium chloride (Baker's analyzed reagent). Unit ionic strength was maintained in all solutions by addition of perchloric acid since the perchlorate ion has little or no tendency to form complexes [Ref. 4].

Tables I and II list the solutions prepared from the tetraaquo-palladium (II) stock and the tetrachloropalladate stock respectively.

## B. ANALYSES

Both of the stock solutions previously described were analyzed for palladium content by precipitating the palladium out as a complex with dimethylglyoxime using the method outlined in Treadwell and Hall [Ref. 18]. To a three or four ml sample of stock solution was added approximately 12 ml of 1% dimethylglyoxime in 95% ethanol. The sample was diluted to about 50ml and allowed to stand approximately 90 minutes. The precipitate was filtered off, dried and weighed.

### 1. Palladous Sulfate (Tetraaquopalladium (II)) Solution

The arithmetic mean of the Pd (II) content of the tetraaquo-palladium (II) stock was 0.0230 g/sample with an average deviation of 0.0003, which is considered good precision. The calculated molarity was 0.0227M.

### 2. Sodium Tetrachloropalladate Solution

The tetrachloropalladate stock was analyzed to have  $0.1266 \pm 0.0002$  g/sample Pd (II) or a calculated molarity of 0.0940M.



### C. EQUIPMENT

Spectral scans were taken on a Beckman model DK-1A recording spectrophotometer utilizing one-cm silica cells. Both the reference and the sample cell compartments were thermostated at 25°C by means of circulating water from a temperature controlled water bath. Temperatures rarely fluctuated more than  $\pm 0.1^\circ\text{C}$ .

### D. ABSORBANCE RUNS

To insure uniformity in procedures, all solutions sat for a minimum of 24 hours before spectral scans were taken even though previous experiments on rates of anation of Pd(II), using both stopped flow methods and hand injection methods with the DK-1A indicate that the rate of the chloride-ion complexing with palladium (II) is rapid enough that thermodynamic stability was reached long before that time. During scanning, the reference and sample solutions were identical except that the reference solution contained no palladium (II). The DK-1A was recalibrated at both zero percent transmittance and 100 percent transmittance prior to running the spectral scan for each sample solution. Data obtained from the scans of the solutions prepared from the tetraaquopalladium (II) stock are contained in Appendix B, and Fig. (1) is a composite of the absorbance scans. Appendix C and Fig. (2) are analogous for solutions prepared from the tetrachloropalladate stock. Specifically, the spectra in figures (1) and (2) are a measure of absorbance vs.  $\text{Cl}^-$  concentration.





TABLE I

SOLUTIONS PREPARED FROM TETRAAQUOPALLADIUM (II) STOCK

The following solutions were all 100ml solutions using the tetra-aquopalladium (II) stock as solvent. Molarities were calculated to three significant figures.

Solution Number	NaCl Added (grams)	Conc Pd (M)	Conc Cl <sup>-</sup> (M)
1	0.1169	0.0227	0.02000
2	0.0234	0.0227	0.00400
3	0.0117	0.0227	0.00200
4	0.0058	0.0227	0.00100
5	0.0012	0.0227	0.00020
6	0.0	0.0227	0.0



FIGURE (1)

The absorbance curves below are for the solutions listed in Table I. As  $\text{Cl}^-$  concentration decreased, the absorbance decreased and the maximum absorbance peak moved to lower wavelengths.

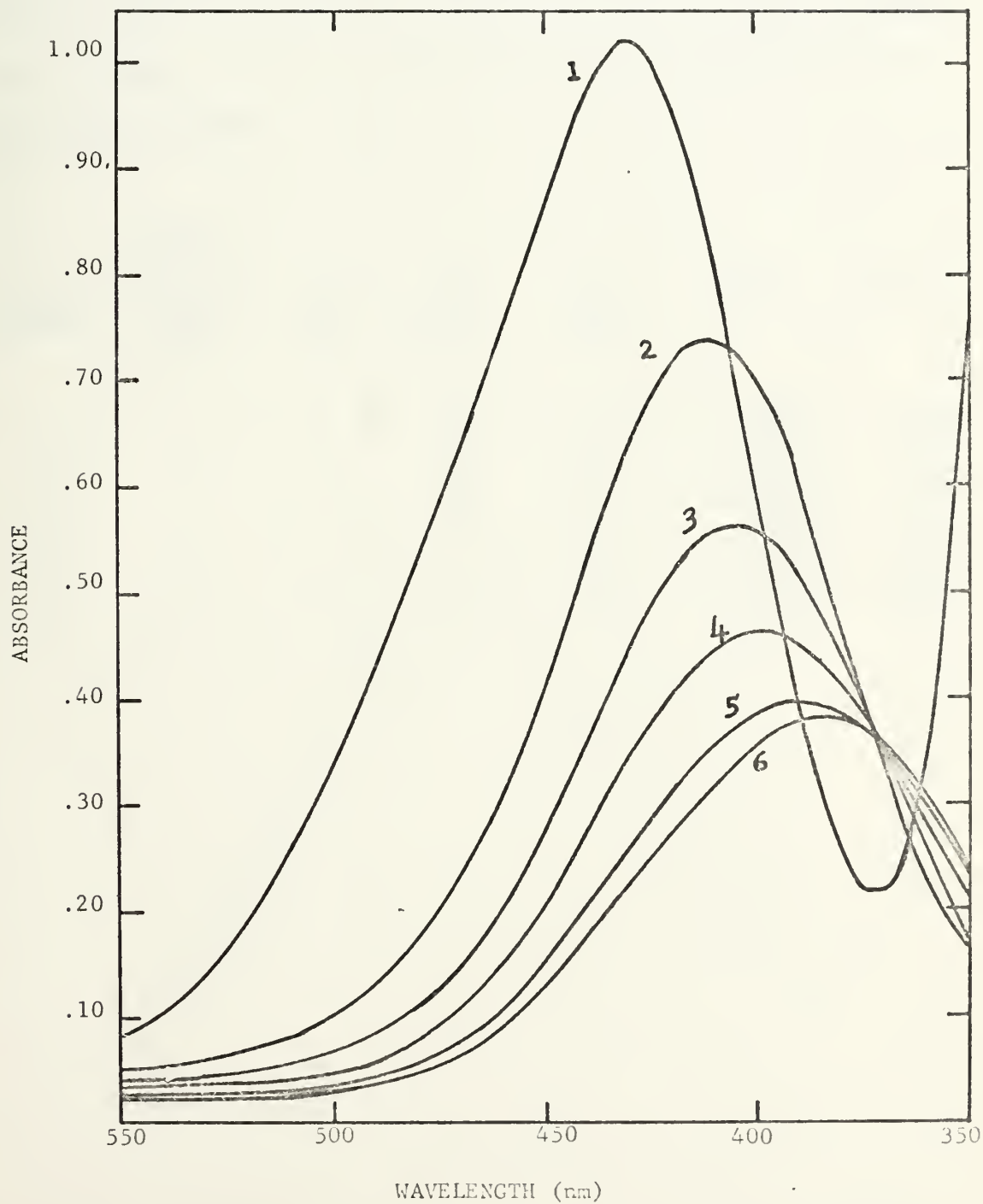




TABLE II

SOLUTIONS PREPARED FROM TETRACHLOROPALLADATE STOCK

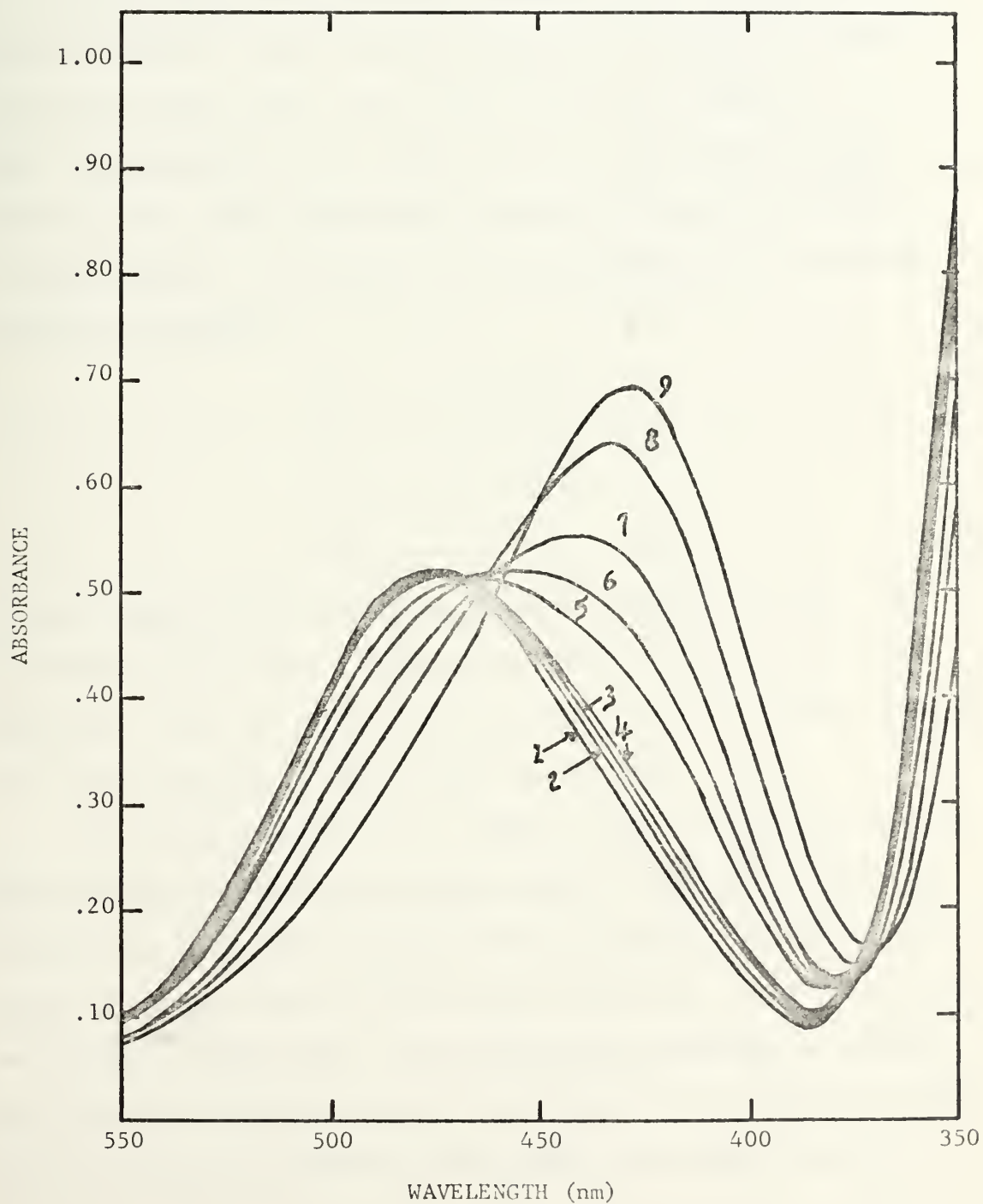
The following solutions were prepared volumetrically by adding listed amounts of the tetrachloropalladate stock, 2.0M NaCl, 1.0M HCl, and 1.0M HClO<sub>4</sub>. Pd and Cl<sup>-</sup> concentrations were calculated to three significant figures.

Solution Number	Tetra- chloro- palladate Stock (ml)	2.0M NaCl (ml)	1.0M HCl (ml)	1.0M HClO <sub>4</sub> (ml) <sup>4</sup>	Conc Pd	Conc Cl <sup>-</sup>
1	3	3	94	0	0.00282	1.0030
2	3	3	53	41	0.00282	0.5930
3	3	3	34	60	0.00282	0.4030
4	3	3	24	70	0.00282	0.3030
5	3	3	4	90	0.00282	0.1030
6	3	0	6	91	0.00282	0.0630
7	3	0	3	94	0.00282	0.0330
8	3	0	1	96	0.00282	0.0130



FIGURE (2)

The absorbance curves below are for solutions listed in Table II. As  $\text{Cl}^-$  concentration decreased, the absorbance increased and the maximum absorbance peak moved to lower wavelengths.





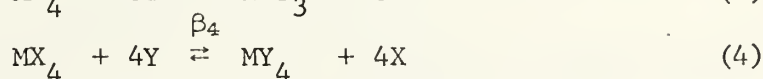
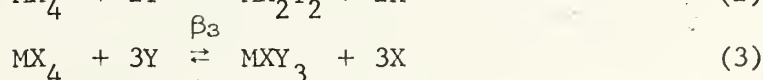
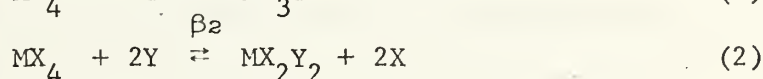
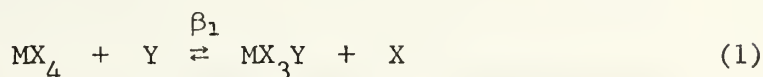


### III. TREATMENT OF DATA AND RESULTS

#### A. DETERMINATION OF STABILITY CONSTANTS

##### 1. General

To determine the stability constants of the  $\text{Cl}^-$  complexes of  $\text{Pd(II)}$ , a method of curve fitting developed by Srivastava and Newman [Ref. 19] in their study of  $\text{Br}^-$  and  $\text{Cl}^-$  complexes of  $\text{Pd(II)}$  was utilized. In the general case, where X and Y are monodentate ligands and M is a metal which forms square-planar complexes, the formation of mixed complexes of the system may be represented by the following replacement reactions:



In the situation where X and Y are the only complexing ligands, the equilibria of the entire system can be categorized by starting with either  $\text{MX}_4$  or  $\text{MY}_4$  and looking at the replacement of two ligands. Therefore, only reactions (1) and (2) need be studied.

The isosbestic point ( $\lambda = 372\text{nm}$ ) in Fig. (1) indicated that no more than two absorbing species were present in the solutions being scanned [Ref. 20]. These species would be  $\text{Pd(OH}_2)_4^{2+}$  and  $\text{Pd(OH}_2)_3\text{Cl}^+$ . Similarly for the other end of the system (Fig. (2)) the species present were  $\text{PdCl}_4^{2-}$  and  $\text{PdCl}_3(\text{OH}_2)^-$ . By sufficiently increasing the ligand ratio, R, the absorbance spectrum moved away from the isosbestic point which indicated the formation of  $\text{PdCl}_2(\text{OH}_2)_2$  for either case. The



ligand ratio was defined as the ratio of Y to X, such that when starting with  $\text{Pd}(\text{OH}_2)_4^{2+}$ ,  $R = [\text{Cl}^-]$ , and when starting with  $\text{PdCl}_4^{2-}$ ,  $R = 1/[\text{Cl}^-]$ .

## 2. First Step Constants

When just two absorbing species are in equilibrium with each other, then from Beer's Law and the additive property of absorbances, the total absorbance of the two species can be shown [Ref. 19] to be

$$A = \frac{A_o + A_1\beta_1 R}{1 + \beta_1 R}$$

where,  $A$  = measured absorbance of the equilibrium mixture,  
 $A_o$  = absorbance of the parent complex ( $\text{MX}_4$  or  $\text{MY}_4$ )  
provided all Pd were of that form,  
 $A_1$  = absorbance of the second complex ( $\text{MX}_3\text{Y}$  or  $\text{MY}_3\text{X}$ )  
provided all Pd were of that form,  
 $\beta_1$  = formation constant, reaction (1),  
and  $R$  = ligand ratio.

By defining a term,  $\Delta = A_o - A_1$ , and algebraically manipulating the absorbance equation above, the following expression was obtained:

$$\Delta(1 + \beta_1 R)^{-1} = A - A_1.$$

A second variable was defined as  $V = 1 + \beta_1 R$ , so that upon substitution into the preceding equation, the following were found:

$$\Delta V^{-1} = A - A_1$$

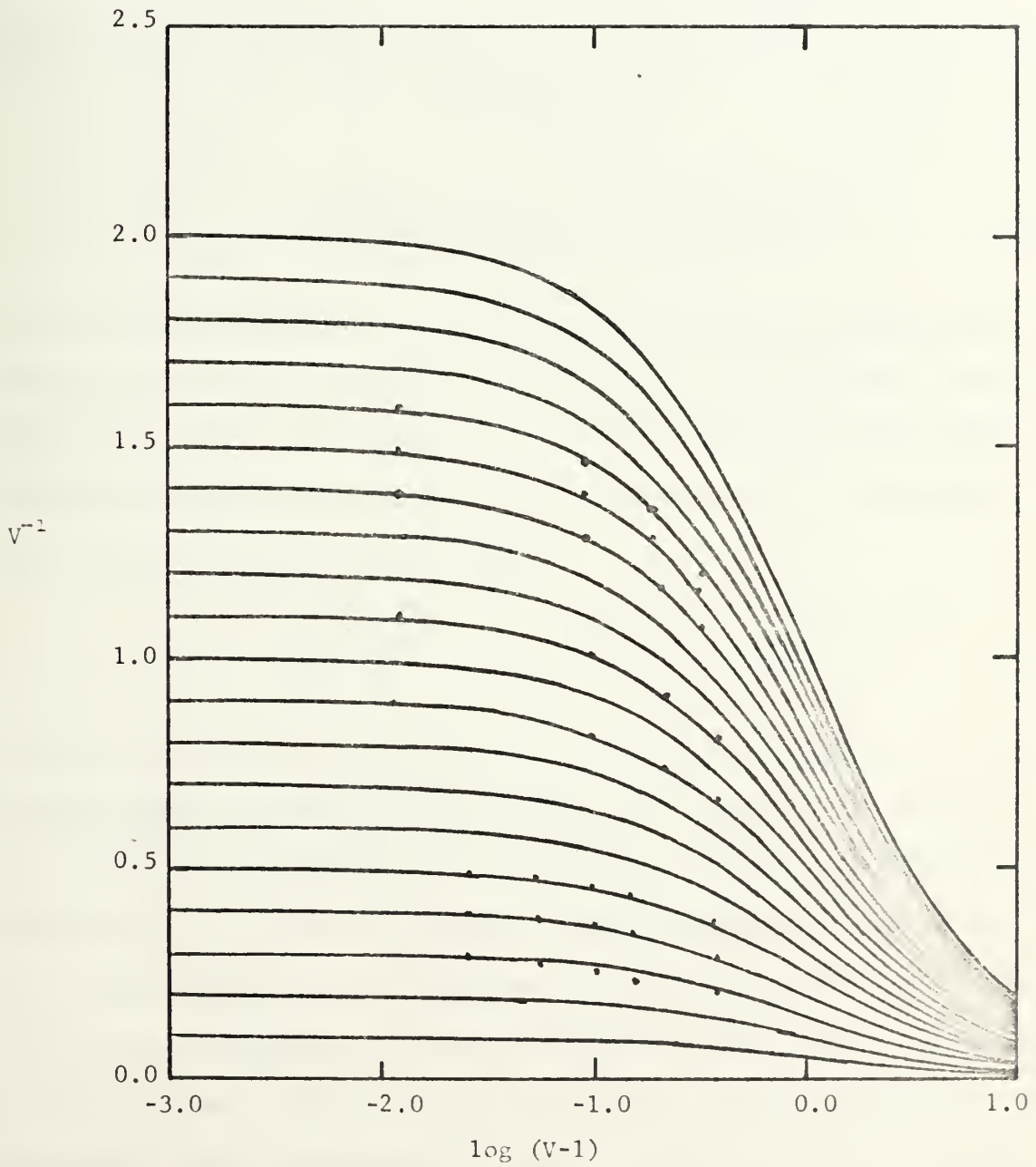
and  $\log(V-1) = \log R + \log \beta_1$ .

A set of normalized curves,  $\Delta V^{-1}$  vs.  $\log(V-1)$  was calculated (Appendix A) by assuming various values for  $\Delta$  and  $V$ . The values were plotted in Fig. (3). Plots of  $A$  vs.  $\log R$  from Appendices B and C were then constructed and superimposed on that normalized curve which gave the best fit.  $\log \beta_1$  was obtained from the translation in the abscissa and  $A_1$  from the translation in the ordinate. The values obtained from the plots at various wavelengths were in close agreement. Each value obtained was weighted equally and a simple average taken to obtain the



FIGURE (3)

The curves below are plotted from the data in Appendix A. The data from appendices B and C were fitted to these curves to determine values for  $A_1$  and  $\log \beta_1$ .





reported value. The two first step values obtained were

$$\log \beta_1 = \log K_1 = [\text{PdCl}(\text{OH}_2)_3^+]/[\text{Pd}(\text{OH}_2)_4^{2+}][\text{Cl}^-] = 1.887 \pm 0.028, \text{ and}$$

$$\log \beta_1' = \log K_4 = [\text{PdCl}_4^{2-}]/[\text{PdCl}_3(\text{OH}_2)^-][\text{Cl}^-] = 1.441 \pm 0.054.$$

### 3. Second Step Constants

As shown previously, when R was changed sufficiently, a third complex,  $\text{PdCl}_2(\text{OH}_2)_2$ , was formed and was in equilibrium with the other two complexes. Due to the presence of this new complex, more terms appear in the expression for the absorbance as follows:

$$A = \frac{A_o + A_1\beta_1R + A_2\beta_2R^2}{1 + \beta_1R + \beta_2R^2}$$

where,  $A_2$  = absorbance of the third complex ( $\text{MX}_2\text{Y}_2$ )  
provided all Pd were of that form,  
and  $\beta_2$  = formation constant, reaction (2).

Of the methods available to solve for the individual absorbances and formation constants, including solution of sets of simultaneous equations, the method that allowed for the easiest handling of absorbance data was to manipulate the equation into the equation of a straight line. The equation [Ref. 19] became

$$\frac{(A - A_2)R^2}{(A_o - A)} = 1/\beta_2 + \frac{R(A_1 - A)}{(A_o - A)} \beta_1/\beta_2.$$

The values of  $A_2$  were assumed and the left hand term calculated using a Hewlett-Packard Calculator Model 9100A. The values for the left hand term and values calculated for  $R(A_1 - A)/(A_o - A)$  using the previously determined  $A_1$  were then entered into a linear regression program [Ref. 21]. The output from the program was a correlation coefficient,  $r$ , and the slope and intercept of the corresponding straight line. The values yielding the best correlation were used and  $\beta_2$  was calculated from the intercept value. A check was also made on previously calculated values





of  $\beta_1$  by using the slope and the value just obtained for  $\beta_2$ . The values obtained for  $\log K_1$  by the two methods agreed within 4% and for  $\log K_4$  within 6%.

The method of mathematical handling of the data for the determination of the second step stability constants dictated a statistical adjustment of the values calculated. Naturally the data with the better correlation coefficient should be weighted more heavily than those not having good correlation. Therefore, the data were weighted statistically as follows:

$$\log \beta_2 = \frac{\sum_i (1/(1 - r_i^2)) (\log \beta_{2i})}{\sum_i 1/(1 - r_i^2)}$$

where,  $r_i$  = correlation coefficient,  
and  $\log \beta_{2i}$  = value of  $\log \beta_2$  corresponding to data  
yielding correlation coefficient  $r_i$ .

The stepwise formation constants were then calculated from  $\log \beta_2$  using the equation

$$\log K_2 = \log \beta_2 - \log K_1.$$

Values obtained for the second step formation constants were

$$\log K_2 = [\text{PdCl}_2(\text{OH}_2)_2]/[\text{PdCl}(\text{OH}_2)_3^+][\text{Cl}^-] = 2.070 \pm 0.028 \text{ and}$$

$$\log K_3 = [\text{PdCl}_3(\text{OH}_2)^-]/[\text{PdCl}_2(\text{OH}_2)_2][\text{Cl}^-] = 2.417 \pm 0.054.$$

## B. ABSORBANCES AND INDIVIDUAL CONSTANTS

The absorbances obtained as a function of wavelength and the individual stability constants calculated at various wavelengths are tabulated in Appendix D.



#### IV. DISCUSSION

##### A. ESTIMATED STATISTICAL VALUES

Values of  $K_i$ , as  $i$  increases, are expected to decrease steadily provided there are only slight changes in the metal-ligand bond energies [Ref. 1]. This expectation is based on several factors including steric hindrance, coulombic factors, and statistical factors. Steric hindrance should not have had a great impact on the values obtained for the system studied in this research because even though the  $\text{Cl}^-$  is a large ion, it does not have the bulk of the  $\text{H}_2\text{O}$  molecule it replaced. Coulombic factors would definitely cause a decrease in progressive values of the  $K_i$ 's in this system because as each successive  $\text{Cl}^-$  is bonded to the  $\text{Pd(II)}$ , the charge on the complex would become less attractive to another  $\text{Cl}^-$ . Statistical factors are somewhat more involved than the qualitative discussions rendered steric hindrance and coulombic factors. In the case studied, the coordination number of the  $\text{Pd(II)}$  was four and remained so throughout the successive replacement reactions. When the coordination number remains the same, the series can be represented, in the general form, as  $\text{M(OH}_2)_N \dots \text{M(OH}_2)_{N-n} \text{X}_n \dots \text{MX}_n$ . The  $\text{M(OH}_2)_{N-n} \text{X}_n$  species has  $n$  locations from which to lose a ligand, whereas the next species in the series,  $\text{M(OH}_2)_{N-n+1} \text{X}_{n+1}$ , would have  $N-n+1$  sites at which to gain a ligand. Therefore, the probability of the ligand replacement taking place is proportional to  $(N-n+1)/n$ . Similarly, the probability of the next replacement taking place is proportional to  $(N-n)/(n+1)$ . Therefore, on statistical considerations alone, a ratio of statistical constants can be shown to be:



$$\frac{K_{n+1}}{K_n} = \frac{n(N-n)}{(n+1)(N-n+1)} \quad [\text{Ref. 1}].$$

The values tabulated below are comparisons of the estimated statistical values and the experimental values from this work.

	Statistical	Experimental
$K_2/K_1$	0.375	1.52
$K_3/K_2$	0.444	1.85
$K_4/K_3$	0.375	0.106

## B. COMPARISONS

The tremendous deviations in statistical and experimental values, in the first two cases, led to other investigations which revealed even more anomalies. The value for  $K_1$  became suspect when it was discovered that even though the absorbance curve for the starting material fit the general shape and  $\lambda_{\text{max}}$  of a  $\text{Pd}(\text{OH}_2)_4^{2+}$  spectrum [Refs. 11,16],  $\epsilon$  for the species at  $A_{\text{max}} = 384\text{nm}$  was only 19 as compared to the generally accepted value of 80 [Ref. 11]. Additionally, the value found for  $K_1$  was extremely low compared to the values reported by Shchukarev et al [Ref. 14], Burger [Ref. 13], Weed [Ref. 12], and Droll [Ref. 10].

The value reported by Droll is, however, considered high in light of work reported by Rasmussen and Jørgensen [Ref. 11], which included a study of the replacement of  $\text{Pd}(\text{II})$  by  $\text{Hg}(\text{II})$  to form  $\text{HgCl}_4^{2-}$ . Since the replacement goes almost to completion, and the values of  $\log K_1$  and  $\log K_2$  for  $\text{Hg}(\text{II})$  chloro complexes are 6.74 and 6.48, then  $\log K_1$  for the  $\text{Pd}(\text{II})$  system must be less than 6. It is also suspected that Droll might have had the wrong starting material, since it was prepared from  $\text{PdO}$ . Rasmussen and Jørgensen have determined that solutions prepared thus from  $\text{PdO}$  in  $\text{HClO}_4$  have higher extinction and develop a dark decomposition product that precipitates out with time.



Early work in this research included a method of estimating the location of absorption maxima of the various chloro complexes of Pd(II). The method employed was to plot wavelength vs wave number and assume an equidistant relationship between  $A_{\max}$  peaks for the species with respect to wave number. The wave number values obtained were then converted to wavelength via the plot. The estimated locations and the experimentally determined locations are listed below.

	Estimated	Experimental
$\text{PdCl}_4^{2-}$	475nm	475nm
$\text{PdCl}_3(\text{OH}_2)^-$	447nm	430nm
$\text{PdCl}_2(\text{OH}_2)_2$	423nm	430nm, 455nm
$\text{PdCl}(\text{OH}_2)_3^+$	401nm	420nm
$\text{Pd}(\text{OH}_2)_4^{2+}$	381nm	384nm

Two values for the location of  $A_{\max}$  for the  $\text{PdCl}_2(\text{OH}_2)_2$  species were calculated since it was approached from both ends of the system. Two anomalies exist in the values -- first, they do not agree with each other, and second, one of the values would have the  $A_{\max}$  located between the absorbance maxima of  $\text{PdCl}_4^{2-}$  and  $\text{PdCl}_3(\text{OH}_2)^-$  which is most unlikely. A final irregularity was that the value for  $K_2$  was also very low as compared to values of the same workers cited before (Shchukarev, Burger, Weed, and Droll). This anomaly can be explained on the basis that the values of  $A_1$  which were obtained using the suspect  $\text{Pd}(\text{OH}_2)_4^{2+}$  starting material were used in the calculations of  $\beta_2$ , thereby compounding the error. The values on the other end of the system appear to be quite satisfactory in comparison to the values of the other workers and in comparison to the statistically predicted values. Additionally, the  $\epsilon_{\max}$  for the  $\text{PdCl}_4^{2-}$  starting material was 173 which compares favorably with the 159 value reported by Cohen and Davidson [Ref. 17]. The





location of  $A_{\max}$  for the  $\text{PdCl}_3(\text{OH}_2)^-$  species did not appear at the wavelength predicted by the wavelength vs. wave number plot, but that prediction was only a first approximation.

### C. CONCLUSION

Little can be discussed about the values reported by Burger and by Weed because their papers were not available. Shchukarev's report appears to give few details about experimental procedure. A value for  $K_4$  was reported by Schwab and Rund [Ref. 22], reported as the equilibrium of the tetrachloro species with the solvated species, the equilibrium being a part of a proposed kinetic mechanism for the replacement of two chloride ions by the bidentate ligand, 2,2' - Bipyridyl. This was calculated, along with two rate constants, by solving sets of simultaneous rate equations utilizing  $k_{\text{obsd}}$  values for the above mentioned bipy replacement. The value reported was  $3.2 \times 10^{-3}$  or  $\log K_4 = 2.5$ , which is, like Droll's, high compared to the other values for  $K_4$ .

Values of  $K_4$  and  $K_3$  obtained from this research appear to be reliable based on comparisons with values of other workers, the agreement among the various values obtained from each data set, and the comparison to the statistical estimations.

On the other hand, further work is definitely needed in the determination of values for  $K_2$  and  $K_1$ . As pointed out there is a great deal of doubt as to the reliability of these two values as well as the locations of  $A_{\max}$  for the middle three species of the series. The values are suspect based primarily on the fact that possibly the starting material was not  $\text{Pd}(\text{OH}_2)_4^{2+}$ . It is considered that the method of preparation of  $\text{Pd}(\text{OH}_2)_4^{2+}$  (boiling  $\text{Pd}(\text{NO}_3)_2$  in concentrated  $\text{H}_2\text{SO}_4$ ) is the most convenient. It should also be pointed out that since  $\text{NO}_3^-$  is a



good absorber in this spectral region, if any  $\text{NO}_3^-$  happened to not be driven off in the boiling process, the resulting solution of  $\text{PdSO}_4$  in  $\text{HClO}_4$  would yield a larger  $\epsilon_{\text{max}}$  than the  $\epsilon_{\text{max}}$  obtained in this work. Additional information of interest would be to calculate the  $\epsilon$ 's for all of the species, once all of the  $K_i$ 's and  $A_i$ 's had been obtained and checked. The method of calculation would be Beer's Law as it is written in the introduction of this report. The advantage of calculating the  $\epsilon$ 's would be the ability to reconstruct the absorbance curves of the various individual species of the system. The method of checking the values obtained for  $K_1$  through  $K_4$  and  $A_0$  through  $A_4$  would be to substitute corresponding values for  $\beta_1$  through  $\beta_4$  and  $A_0$  through  $A_4$  into the absorbance equation described in the treatment of data and results section and reconstruct the curves in Figs. (1) and (2).



## APPENDIX A

### NORMALIZED CURVES DATA

This Appendix contains all calculated data used in plotting the normalized curves of Fig. (3). Curves for  $\Delta = 0.1$  and  $\Delta = -0.1$  are mirror images of each other across the horizontal ( $\log (V-1)$ ) axis.

$$\Delta = 0.1$$

V	$V^{-1}$	$\Delta V^{-1}$	V-1	$\log (V-1)$
1.01	0.9901	0.099	0.01	-2.000
1.02	0.9804	0.098	0.02	-1.699
1.03	0.9709	0.097	0.03	-1.523
1.04	0.9615	0.096	0.04	-1.398
1.05	0.9524	0.095	0.05	-1.301
1.06	0.9434	0.094	0.06	-1.222
1.07	0.9346	0.094	0.07	-1.155
1.08	0.9259	0.093	0.08	-1.097
1.09	0.9174	0.092	0.09	-1.046
1.10	0.9091	0.091	0.10	-1.000
1.12	0.8929	0.089	0.12	-0.921
1.15	0.8696	0.087	0.15	-0.824
1.20	0.8333	0.083	0.20	-0.699
1.25	0.8000	0.080	0.25	-0.602
1.32	0.7576	0.076	0.32	-0.495
1.40	0.7143	0.071	0.40	-0.398
1.50	0.6667	0.067	0.50	-0.301
1.63	0.6135	0.061	0.63	-0.201
1.79	0.5587	0.056	0.79	-0.102
2.00	0.5000	0.050	1.00	0.000
3.00	0.3333	0.033	2.00	0.301
4.00	0.2500	0.025	3.00	0.477
5.00	0.2000	0.020	4.00	0.602
6.00	0.1667	0.017	5.00	0.669
7.00	0.1433	0.014	6.00	0.778
8.00	0.1250	0.013	7.00	0.845
9.00	0.1111	0.011	8.00	0.903
10.00	0.1000	0.010	9.00	0.954



$$\Delta = 0.2$$

$V$	$V^{-1}$	$\Delta V^{-1}$	$V-1$	$\log (V-1)$
1.01	0.9901	0.198	0.01	-2.000
1.02	0.9804	0.196	0.02	-1.699
1.03	0.9709	0.194	0.03	-1.523
1.04	0.9615	0.192	0.04	-1.398
1.05	0.9524	0.191	0.05	-1.301
1.06	0.9434	0.189	0.06	-1.222
1.07	0.9346	0.187	0.07	-1.155
1.08	0.9259	0.185	0.08	-1.097
1.09	0.9174	0.184	0.09	-1.046
1.10	0.9091	0.182	0.10	-1.000
1.12	0.8929	0.179	0.12	-0.921
1.15	0.8696	0.174	0.15	-0.824
1.20	0.8333	0.167	0.20	-0.699
1.25	0.8000	0.160	0.25	-0.602
1.32	0.7576	0.152	0.32	-0.495
1.40	0.7143	0.143	0.40	-0.398
1.50	0.6667	0.133	0.50	-0.301
1.63	0.6135	0.123	0.63	-0.201
1.79	0.5587	0.112	0.79	-0.102
2.00	0.5000	0.100	1.00	0.000
3.00	0.3333	0.067	2.00	0.301
4.00	0.2500	0.050	3.00	0.477
5.00	0.2000	0.040	4.00	0.602
6.00	0.1667	0.033	5.00	0.699
7.00	0.1433	0.029	6.00	0.778
8.00	0.1250	0.025	7.00	0.845
9.00	0.1111	0.022	8.00	0.903
10.00	0.1000	0.020	9.00	0.954





$$\Delta = 0.3$$

V	$V^{-1}$	$\Delta V^{-1}$	V-1	$\log (V-1)$
1.01	0.9901	0.297	0.01	-2.000
1.02	0.9804	0.294	0.02	-1.699
1.03	0.9709	0.291	0.03	-1.523
1.04	0.9615	0.289	0.04	-1.398
1.05	0.9524	0.286	0.05	-1.301
1.06	0.9434	0.283	0.06	-1.222
1.07	0.9346	0.284	0.07	-1.155
1.08	0.9259	0.278	0.08	-1.097
1.09	0.9174	0.275	0.09	-1.046
1.10	0.9091	0.273	0.10	-1.000
1.12	0.8929	0.268	0.12	-0.921
1.15	0.8696	0.261	0.15	-0.824
1.20	0.8333	0.250	0.20	-0.699
1.25	0.8000	0.240	0.25	-0.602
1.32	0.7576	0.228	0.32	-0.495
1.40	0.7143	0.214	0.40	-0.398
1.50	0.6667	0.200	0.50	-0.301
1.63	0.6135	0.184	0.63	-0.201
1.79	0.5587	0.167	0.79	-0.102
2.00	0.5000	0.150	1.00	0.000
3.00	0.3333	0.100	2.00	0.301
4.00	0.2500	0.075	3.00	0.477
5.00	0.2000	0.060	4.00	0.602
6.00	0.1667	0.050	5.00	0.699
7.00	0.1433	0.043	6.00	0.778
8.00	0.1250	0.038	7.00	0.845
9.00	0.1111	0.033	8.00	0.903
10.00	0.1000	0.030	9.00	0.954



$$\Delta = 0.4$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	0.396	0.01	-2.000
1.02	0.9804	0.392	0.02	-1.699
1.03	0.9709	0.388	0.03	-1.523
1.04	0.9615	0.385	0.04	-1.398
1.05	0.9524	0.381	0.05	-1.301
1.06	0.9434	0.377	0.06	-1.222
1.07	0.9346	0.374	0.07	-1.155
1.08	0.9259	0.370	0.08	-1.097
1.09	0.9174	0.367	0.09	-1.046
1.10	0.9091	0.364	0.10	-1.000
1.12	0.8929	0.357	0.12	-0.921
1.15	0.8696	0.348	0.15	-0.824
1.20	0.8333	0.333	0.20	-0.699
1.25	0.8000	0.320	0.25	-0.602
1.32	0.7576	0.303	0.32	-0.495
1.40	0.7143	0.286	0.40	-0.398
1.50	0.6667	0.267	0.50	-0.301
1.63	0.6135	0.245	0.63	-0.201
1.79	0.5587	0.224	0.79	-0.102
2.00	0.5000	0.200	1.00	0.000
3.00	0.3333	0.133	2.00	0.301
4.00	0.2500	0.100	3.00	0.477
5.00	0.2000	0.080	4.00	0.602
6.00	0.1667	0.067	5.00	0.699
7.00	0.1433	0.057	6.00	0.778
8.00	0.1250	0.050	7.00	0.845
9.00	0.1111	0.044	8.00	0.903
10.00	0.1000	0.040	9.00	0.954



$$\Delta = 0.5$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	0.495	0.01	-2.000
1.02	0.9804	0.490	0.02	-1.699
1.03	0.9709	0.485	0.03	-1.523
1.04	0.9615	0.481	0.04	-1.398
1.05	0.9524	0.476	0.05	-1.301
1.06	0.9434	0.472	0.06	-1.222
1.07	0.9346	0.467	0.07	-1.155
1.08	0.9259	0.463	0.08	-1.097
1.09	0.9174	0.459	0.09	-1.046
1.10	0.9091	0.455	0.10	-1.000
1.12	0.8929	0.447	0.12	-0.921
1.15	0.8696	0.435	0.15	-0.824
1.20	0.8333	0.417	0.20	-0.699
1.25	0.8000	0.400	0.25	-0.602
1.32	0.7576	0.379	0.32	-0.495
1.40	0.7143	0.357	0.40	-0.398
1.50	0.6667	0.333	0.50	-0.301
1.63	0.6135	0.307	0.63	-0.201
1.79	0.5587	0.279	0.79	-0.102
2.00	0.5000	0.250	1.00	0.000
3.00	0.3333	0.167	2.00	0.301
4.00	0.2500	0.125	3.00	0.477
5.00	0.2000	0.100	4.00	0.602
6.00	0.1667	0.084	5.00	0.699
7.00	0.1433	0.072	6.00	0.778
8.00	0.1250	0.063	7.00	0.845
9.00	0.1111	0.056	8.00	0.903
10.00	0.1000	0.050	9.00	0.954



$$\Delta = 0.6$$

V	$V^{-1}$	$\Delta V^{-1}$	V-1	$\log (V-1)$
1.01	0.9901	0.594	0.01	-2.000
1.02	0.9804	0.588	0.02	-1.699
1.03	0.9709	0.583	0.03	-1.523
1.04	0.9615	0.577	0.04	-1.398
1.05	0.9524	0.572	0.05	-1.301
1.06	0.9434	0.566	0.06	-1.222
1.07	0.9346	0.561	0.07	-1.155
1.08	0.9259	0.556	0.08	-1.097
1.09	0.9174	0.550	0.09	-1.046
1.10	0.9091	0.546	0.10	-1.000
1.12	0.8929	0.536	0.12	-0.921
1.15	0.8696	0.522	0.15	-0.824
1.20	0.8333	0.500	0.20	-0.699
1.25	0.8000	0.480	0.25	-0.602
1.32	0.7576	0.455	0.32	-0.495
1.40	0.7143	0.429	0.40	-0.398
1.50	0.6667	0.400	0.50	-0.301
1.63	0.6135	0.368	0.63	-0.201
1.79	0.5587	0.335	0.79	-0.102
2.00	0.5000	0.300	1.00	0.000
3.00	0.3333	0.200	2.00	0.301
4.00	0.2500	0.150	3.00	0.477
5.00	0.2000	0.120	4.00	0.602
6.00	0.1667	0.100	5.00	0.699
7.00	0.1433	0.086	6.00	0.778
8.00	0.1250	0.075	7.00	0.845
9.00	0.1111	0.067	8.00	0.903
10.00	0.1000	0.060	9.00	0.954





$$\Delta = 0.7$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	0.693	0.01	-2.000
1.02	0.9804	0.686	0.02	-1.699
1.03	0.9709	0.680	0.03	-1.533
1.04	0.9615	0.673	0.04	-1.398
1.05	0.9524	0.667	0.05	-1.301
1.06	0.9434	0.660	0.06	-1.222
1.07	0.9346	0.654	0.07	-1.155
1.08	0.9259	0.648	0.08	-1.097
1.09	0.9174	0.642	0.09	-1.046
1.10	0.9091	0.636	0.10	-1.000
1.12	0.8929	0.625	0.12	-0.921
1.15	0.8696	0.609	0.15	-0.824
1.20	0.8333	0.583	0.20	-0.699
1.25	0.8000	0.560	0.25	-0.602
1.32	0.7576	0.530	0.32	-0.495
1.40	0.7143	0.500	0.40	-0.398
1.50	0.6667	0.467	0.50	-0.301
1.63	0.6135	0.430	0.63	-0.201
1.79	0.5587	0.391	0.79	-0.102
2.00	0.5000	0.350	1.00	0.000
3.00	0.3333	0.233	2.00	0.301
4.00	0.2500	0.175	3.00	0.477
5.00	0.2000	0.140	4.00	0.602
6.00	0.1667	0.117	5.00	0.699
7.00	0.1433	0.100	6.00	0.778
8.00	0.1250	0.088	7.00	0.845
9.00	0.1111	0.078	8.00	0.903
10.00	0.1000	0.070	9.00	0.954



$$\Delta = 0.8$$

V	$V^{-1}$	$\Delta V^{-1}$	V-1	$\log (V-1)$
1.01	0.9901	0.792	0.01	-2.000
1.02	0.9804	0.784	0.02	-1.699
1.03	0.9709	0.777	0.03	-1.523
1.04	0.9615	0.769	0.04	-1.398
1.05	0.9524	0.762	0.05	-1.301
1.06	0.9434	0.755	0.06	-1.222
1.07	0.9346	0.748	0.07	-1.155
1.08	0.9259	0.741	0.08	-1.097
1.09	0.9174	0.734	0.09	-1.046
1.10	0.9091	0.727	0.10	-1.000
1.12	0.8929	0.714	0.12	-0.921
1.15	0.8696	0.696	0.15	-0.824
1.20	0.8333	0.667	0.20	-0.699
1.25	0.8000	0.640	0.25	-0.602
1.32	0.7576	0.606	0.32	-0.495
1.40	0.7143	0.571	0.40	-0.398
1.50	0.6667	0.533	0.50	-0.301
1.63	0.6135	0.491	0.63	-0.201
1.79	0.5587	0.447	0.79	-0.102
2.00	0.5000	0.400	1.00	0.000
3.00	0.3333	0.266	2.00	0.301
4.00	0.2500	0.200	3.00	0.477
5.00	0.2000	0.160	4.00	0.602
6.00	0.1667	0.134	5.00	0.699
7.00	0.1433	0.114	6.00	0.778
8.00	0.1250	0.100	7.00	0.845
9.00	0.1111	0.089	8.00	0.903
10.00	0.1000	0.080	9.00	0.954



$$\Delta = 0.9$$

V	$V^{-1}$	$\Delta V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.891	0.01	-2.000
1.02	0.9804	0.882	0.02	-1.699
1.03	0.9709	0.874	0.03	-1.523
1.04	0.9615	0.865	0.04	-1.398
1.05	0.9524	0.857	0.05	-1.301
1.06	0.9434	0.849	0.06	-1.222
1.07	0.9346	0.841	0.07	-1.155
1.08	0.9259	0.833	0.08	-1.097
1.09	0.9174	0.826	0.09	-1.046
1.10	0.9091	0.818	0.10	-1.000
1.12	0.8929	0.804	0.12	-0.921
1.15	0.8696	0.783	0.15	-0.824
1.20	0.8333	0.750	0.20	-0.699
1.25	0.8000	0.720	0.25	-0.602
1.32	0.7576	0.682	0.32	-0.495
1.40	0.7143	0.643	0.40	-0.398
1.50	0.6667	0.600	0.50	-0.301
1.63	0.6135	0.552	0.63	-0.201
1.79	0.5587	0.503	0.79	-0.102
2.00	0.5000	0.450	1.00	0.000
3.00	0.3333	0.300	2.00	0.301
4.00	0.2500	0.225	3.00	0.477
5.00	0.2000	0.180	4.00	0.602
6.00	0.1667	0.150	5.00	0.699
7.00	0.1433	0.129	6.00	0.778
8.00	0.1250	0.113	7.00	0.845
9.00	0.1111	0.100	8.00	0.903
10.00	0.1000	0.090	9.00	0.954



$$\Delta = 1.0$$

$V$	$V^{-1}$	$\Delta V^{-1}$	$V-1$	$\log (V-1)$
1.01	0.9901	0.990	0.01	-2.000
1.02	0.9804	0.980	0.02	-1.699
1.03	0.9709	0.971	0.03	-1.523
1.04	0.9615	0.962	0.04	-1.398
1.05	0.9524	0.952	0.05	-1.301
1.06	0.9434	0.943	0.06	-1.222
1.07	0.9346	0.935	0.07	-1.155
1.08	0.9259	0.926	0.08	-1.097
1.09	0.9174	0.917	0.09	-1.046
1.10	0.9091	0.909	0.10	-1.000
1.12	0.8929	0.893	0.12	-0.921
1.15	0.8696	0.870	0.15	-0.824
1.20	0.8333	0.833	0.20	-0.699
1.25	0.8000	0.800	0.25	-0.602
1.32	0.7576	0.758	0.32	-0.495
1.40	0.7143	0.714	0.40	-0.398
1.50	0.6667	0.667	0.50	-0.301
1.63	0.6135	0.614	0.63	-0.201
1.79	0.5587	0.559	0.79	-0.102
2.00	0.5000	0.500	1.00	0.000
3.00	0.3333	0.333	2.00	0.301
4.00	0.2500	0.250	3.00	0.477
5.00	0.2000	0.200	4.00	0.602
6.00	0.1667	0.167	5.00	0.699
7.00	0.1433	0.143	6.00	0.778
8.00	0.1250	0.125	7.00	0.845
9.00	0.1111	0.111	8.00	0.903
10.00	0.1000	0.100	9.00	0.954





$$\Delta = 1.1$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.089	0.01	-2.000
1.02	0.9804	1.078	0.02	-1.699
1.03	0.9709	1.068	0.03	-1.523
1.04	0.9615	1.058	0.04	-1.398
1.05	0.9524	1.048	0.05	-1.301
1.06	0.9434	1.038	0.06	-1.222
1.07	0.9346	1.028	0.07	-1.155
1.08	0.9259	1.019	0.08	-1.097
1.09	0.9174	1.009	0.09	-1.046
1.10	0.9091	1.000	0.10	-1.000
1.12	0.8929	0.982	0.12	-0.921
1.15	0.8696	0.957	0.15	-0.824
1.20	0.8333	0.917	0.20	-0.699
1.25	0.8000	0.880	0.25	-0.602
1.32	0.7576	0.833	0.32	-0.495
1.40	0.7143	0.786	0.40	-0.398
1.50	0.6667	0.733	0.50	-0.301
1.63	0.6135	0.675	0.63	-0.201
1.79	0.5587	0.615	0.79	-0.102
2.00	0.5000	0.550	1.00	0.000
3.00	0.3333	0.366	2.00	0.301
4.00	0.2500	0.275	3.00	0.477
5.00	0.2000	0.220	4.00	0.602
6.00	0.1667	0.184	5.00	0.699
7.00	0.1433	0.157	6.00	0.778
8.00	0.1250	0.138	7.00	0.845
9.00	0.1111	0.122	8.00	0.903
10.00	0.1000	0.110	9.00	0.954



$$\Delta = 1.2$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.188	0.01	-2.000
1.02	0.9804	1.177	0.02	-1.699
1.03	0.9709	1.165	0.03	-1.523
1.04	0.9615	1.154	0.04	-1.398
1.05	0.9524	1.143	0.05	-1.301
1.06	0.9434	1.132	0.06	-1.222
1.07	0.9346	1.122	0.07	-1.155
1.08	0.9259	1.111	0.08	-1.097
1.09	0.9174	1.101	0.09	-1.046
1.10	0.9091	1.091	0.10	-1.000
1.12	0.8929	1.072	0.12	-0.921
1.15	0.8696	1.044	0.15	-0.824
1.20	0.8333	1.000	0.20	-0.699
1.25	0.8000	0.960	0.25	-0.602
1.32	0.7576	0.909	0.32	-0.495
1.40	0.7143	0.857	0.40	-0.398
1.50	0.6667	0.800	0.50	-0.301
1.63	0.6135	0.736	0.63	-0.201
1.79	0.5587	0.670	0.79	-0.102
2.00	0.5000	0.600	1.00	0.000
3.00	0.3333	0.400	2.00	0.301
4.00	0.2500	0.300	3.00	0.477
5.00	0.2000	0.240	4.00	0.602
6.00	0.1667	0.200	5.00	0.699
7.00	0.1433	0.172	6.00	0.778
8.00	0.1250	0.150	7.00	0.845
9.00	0.1111	0.133	8.00	0.903
10.00	0.1000	0.120	9.00	0.954



$$\Delta = 1.3$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.287	0.01	-2.000
1.02	0.9804	1.275	0.02	-1.699
1.03	0.9709	1.262	0.03	-1.523
1.04	0.9615	1.250	0.04	-1.398
1.05	0.9524	1.238	0.05	-1.301
1.06	0.9434	1.226	0.06	-1.222
1.07	0.9346	1.215	0.07	-1.155
1.08	0.9259	1.204	0.08	-1.097
1.09	0.9174	1.193	0.09	-1.046
1.10	0.9091	1.182	0.10	-1.000
1.12	0.8929	1.161	0.12	-0.921
1.15	0.8696	1.131	0.15	-0.824
1.20	0.8333	1.083	0.20	-0.699
1.25	0.8000	1.040	0.25	-0.602
1.32	0.7576	0.985	0.32	-0.495
1.40	0.7143	0.929	0.40	-0.398
1.50	0.6667	0.867	0.50	-0.301
1.63	0.6135	0.798	0.63	-0.201
1.79	0.5587	0.726	0.79	-0.102
2.00	0.5000	0.650	1.00	0.000
3.00	0.3333	0.433	2.00	0.301
4.00	0.2500	0.325	3.00	0.477
5.00	0.2000	0.260	4.00	0.602
6.00	0.1667	0.217	5.00	0.699
7.00	0.1433	0.186	6.00	0.778
8.00	0.1250	0.163	7.00	0.845
9.00	0.1111	0.144	8.00	0.903
10.00	0.1000	0.130	9.00	0.954



$$\Delta = 1.4$$

$V$	$V^{-1}$	$\Delta V^{-1}$	$V-1$	$\log (V-1)$
1.01	0.9901	1.386	0.01	-2.000
1.02	0.9804	1.373	0.02	-1.699
1.03	0.9709	1.359	0.03	-1.523
1.04	0.9615	1.346	0.04	-1.398
1.05	0.9524	1.333	0.05	-1.301
1.06	0.9434	1.321	0.06	-1.222
1.07	0.9346	1.308	0.07	-1.155
1.08	0.9259	1.296	0.08	-1.097
1.09	0.9174	1.284	0.09	-1.046
1.10	0.9091	1.273	0.10	-1.000
1.12	0.8929	1.250	0.12	-0.921
1.15	0.8696	1.217	0.15	-0.824
1.20	0.8333	1.167	0.20	-0.699
1.25	0.8000	1.120	0.25	-0.602
1.32	0.7576	1.061	0.32	-0.495
1.40	0.7143	1.000	0.40	-0.398
1.50	0.6667	0.933	0.50	-0.301
1.63	0.6135	0.859	0.63	-0.201
1.79	0.5587	0.782	0.79	-0.102
2.00	0.5000	0.700	1.00	0.000
3.00	0.3333	0.466	2.00	0.301
4.00	0.2500	0.350	3.00	0.477
5.00	0.2000	0.280	4.00	0.602
6.00	0.1667	0.234	5.00	0.699
7.00	0.1433	0.200	6.00	0.778
8.00	0.1250	0.175	7.00	0.845
9.00	0.1111	0.155	8.00	0.903
10.00	0.1000	0.140	9.00	0.954





$$\Delta = 1.5$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.485	0.01	-2.000
1.02	0.9804	1.471	0.02	-1.699
1.03	0.9709	1.456	0.03	-1.523
1.04	0.9615	1.442	0.04	-1.398
1.05	0.9524	1.429	0.05	-1.301
1.06	0.9434	1.415	0.06	-1.222
1.07	0.9346	1.402	0.07	-1.155
1.08	0.9259	1.389	0.08	-1.097
1.09	0.9174	1.376	0.09	-1.046
1.10	0.9091	1.364	0.10	-1.000
1.12	0.8929	1.339	0.12	-0.921
1.15	0.8696	1.304	0.15	-0.824
1.20	0.8333	1.250	0.20	-0.699
1.25	0.8000	1.200	0.25	-0.602
1.32	0.7576	1.136	0.32	-0.495
1.40	0.7143	1.072	0.40	-0.398
1.50	0.6667	1.000	0.50	-0.301
1.63	0.6135	0.920	0.63	-0.201
1.79	0.5587	0.838	0.79	-0.102
2.00	0.5000	0.750	1.00	0.000
3.00	0.3333	0.500	2.00	0.301
4.00	0.2500	0.375	3.00	0.477
5.00	0.2000	0.300	4.00	0.602
6.00	0.1667	0.251	5.00	0.699
7.00	0.1433	0.215	6.00	0.778
8.00	0.1250	0.188	7.00	0.845
9.00	0.1111	0.167	8.00	0.903
10.00	0.1000	0.150	9.00	0.954



$$\Delta = 1.6$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.584	0.01	-2.000
1.02	0.9804	1.569	0.02	-1.699
1.03	0.9709	1.553	0.03	-1.523
1.04	0.9615	1.538	0.04	-1.398
1.05	0.9524	1.524	0.05	-1.301
1.06	0.9434	1.509	0.06	-1.222
1.07	0.9346	1.495	0.07	-1.155
1.08	0.9259	1.481	0.08	-1.097
1.09	0.9174	1.468	0.09	-1.046
1.10	0.9091	1.455	0.10	-1.000
1.12	0.8929	1.429	0.12	-0.921
1.15	0.8696	1.391	0.15	-0.824
1.20	0.8333	1.333	0.20	-0.699
1.25	0.8000	1.280	0.25	-0.602
1.32	0.7576	1.212	0.32	-0.495
1.40	0.7143	1.143	0.40	-0.398
1.50	0.6667	1.067	0.50	-0.301
1.63	0.6135	0.982	0.63	-0.201
1.79	0.5587	0.894	0.79	-0.102
2.00	0.5000	0.800	1.00	0.000
3.00	0.3333	0.533	2.00	0.301
4.00	0.2500	0.400	3.00	0.477
5.00	0.2000	0.320	4.00	0.602
6.00	0.1667	0.267	5.00	0.699
7.00	0.1433	0.229	6.00	0.778
8.00	0.1250	0.200	7.00	0.845
9.00	0.1111	0.178	8.00	0.903
10.00	0.1000	0.160	9.00	0.954



$$\Delta = 1.7$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.683	0.01	-2.000
1.02	0.9804	1.667	0.02	-1.699
1.03	0.9709	1.651	0.03	-1.523
1.04	0.9615	1.634	0.04	-1.398
1.05	0.9524	1.619	0.05	-1.301
1.06	0.9434	1.604	0.06	-1.222
1.07	0.9346	1.589	0.07	-1.155
1.08	0.9259	1.574	0.08	-1.097
1.09	0.9174	1.560	0.09	-1.046
1.10	0.9091	1.546	0.10	-1.000
1.12	0.8929	1.518	0.12	-0.921
1.15	0.8696	1.478	0.15	-0.824
1.20	0.8333	1.417	0.20	-0.699
1.25	0.8000	1.360	0.25	-0.602
1.32	0.7576	1.288	0.32	-0.495
1.40	0.7143	1.214	0.40	-0.398
1.50	0.6667	1.133	0.50	-0.301
1.63	0.6135	1.043	0.63	-0.201
1.79	0.5587	0.950	0.79	-0.102
2.00	0.5000	0.850	1.00	0.000
3.00	0.3333	0.566	2.00	0.301
4.00	0.2500	0.425	3.00	0.477
5.00	0.2000	0.340	4.00	0.602
6.00	0.1667	0.284	5.00	0.699
7.00	0.1433	0.243	6.00	0.778
8.00	0.1250	0.213	7.00	0.845
9.00	0.1111	0.189	8.00	0.903
10.00	0.1000	0.170	9.00	0.954



$$\Delta = 1.8$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.782	0.01	-2.000
1.02	0.9804	1.765	0.02	-1.699
1.03	0.9709	1.748	0.03	-1.523
1.04	0.9615	1.731	0.04	-1.398
1.05	0.9524	1.714	0.05	-1.301
1.06	0.9434	1.698	0.06	-1.222
1.07	0.9346	1.682	0.07	-1.155
1.08	0.9259	1.667	0.08	-1.097
1.09	0.9174	1.651	0.09	-1.046
1.10	0.9091	1.636	0.10	-1.000
1.12	0.8929	1.607	0.12	-0.921
1.15	0.8696	1.565	0.15	-0.824
1.20	0.8333	1.500	0.20	-0.699
1.25	0.8000	1.440	0.25	-0.602
1.32	0.7576	1.364	0.32	-0.495
1.40	0.7143	1.286	0.40	-0.398
1.50	0.6667	1.200	0.50	-0.301
1.63	0.6135	1.104	0.63	-0.201
1.79	0.5587	1.006	0.79	-0.102
2.00	0.5000	0.900	1.00	0.000
3.00	0.3333	0.599	2.00	0.301
4.00	0.2500	0.450	3.00	0.477
5.00	0.2000	0.360	4.00	0.602
6.00	0.1667	0.301	5.00	0.699
7.00	0.1433	0.257	6.00	0.778
8.00	0.1250	0.225	7.00	0.845
9.00	0.1111	0.200	8.00	0.903
10.00	0.1000	0.180	9.00	0.954





$$\Delta = 1.9$$

$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.881	0.01	-2.000
1.02	0.9804	1.863	0.02	-1.699
1.03	0.9709	1.845	0.03	-1.523
1.04	0.9615	1.827	0.04	-1.398
1.05	0.9524	1.810	0.05	-1.301
1.06	0.9434	1.793	0.06	-1.222
1.07	0.9346	1.776	0.07	-1.155
1.08	0.9259	1.759	0.08	-1.097
1.09	0.9174	1.743	0.09	-1.046
1.10	0.9091	1.727	0.10	-1.000
1.12	0.8929	1.697	0.12	-0.921
1.15	0.8696	1.652	0.15	-0.824
1.20	0.8333	1.583	0.20	-0.699
1.25	0.8000	1.520	0.25	-0.602
1.32	0.7576	1.455	0.32	-0.495
1.40	0.7143	1.357	0.40	-0.398
1.50	0.6667	1.267	0.50	-0.301
1.63	0.6135	1.166	0.63	-0.201
1.79	0.5587	1.062	0.79	-0.102
2.00	0.5000	0.950	1.00	0.000
3.00	0.3333	0.633	2.00	0.301
4.00	0.2500	0.475	3.00	0.477
5.00	0.2000	0.380	4.00	0.602
6.00	0.1667	0.317	5.00	0.699
7.00	0.1433	0.272	6.00	0.778
8.00	0.1250	0.238	7.00	0.845
9.00	0.1111	0.211	8.00	0.903
10.00	0.1000	0.190	9.00	0.954



$$\Delta = 2.0$$

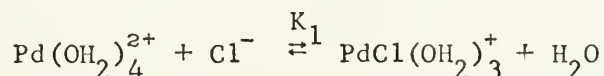
$v$	$v^{-1}$	$\Delta v^{-1}$	$v-1$	$\log (v-1)$
1.01	0.9901	1.980	0.01	-2.000
1.02	0.9804	1.961	0.02	-1.699
1.03	0.9709	1.942	0.03	-1.523
1.04	0.9615	1.923	0.04	-1.398
1.05	0.9524	1.905	0.05	-1.301
1.06	0.9434	1.887	0.06	-1.222
1.07	0.9346	1.869	0.07	-1.155
1.08	0.9259	1.852	0.08	-1.097
1.09	0.9174	1.835	0.09	-1.046
1.10	0.9091	1.818	0.10	-1.000
1.12	0.8929	1.786	0.12	-0.921
1.15	0.8696	1.739	0.15	-0.824
1.20	0.8333	1.667	0.20	-0.699
1.25	0.8000	1.600	0.25	-0.602
1.32	0.7576	1.515	0.32	-0.495
1.40	0.7143	1.429	0.40	-0.398
1.50	0.6667	1.333	0.50	-0.301
1.63	0.6135	1.227	0.63	-0.201
1.79	0.5587	1.117	0.79	-0.102
2.00	0.5000	1.000	1.00	0.000
3.00	0.3333	0.666	2.00	0.301
4.00	0.2500	0.500	3.00	0.477
5.00	0.2000	0.400	4.00	0.602
6.00	0.1667	0.334	5.00	0.699
7.00	0.1433	0.286	6.00	0.778
8.00	0.1250	0.250	7.00	0.845
9.00	0.1111	0.222	8.00	0.903
10.00	0.1000	0.200	9.00	0.954



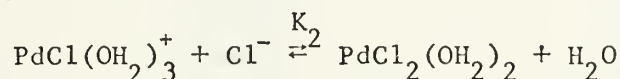
## APPENDIX B

### ABSORBANCE DATA FOR DETERMINING $K_1$ AND $K_2$

The absorbance data in this appendix came from the spectra of Fig. (1) and was fitted to the normalized curves in Fig (3) to give values of  $K_1$  for the equilibrium:



Additionally, the data was used to determine values for  $K_2$  for the equilibrium:



All absorbances were for solutions of unit ionic strength,  $[\text{Pd}] = 0.0227$ , and  $T = 25.0^\circ\text{C}$ . Concentrations of  $\text{Cl}^-$  were accurate to three significant figures and so, therefore, was the ligand ratio,  $R$ .  $\log R$  is reported to three decimal places. Absorbances are accurate to  $\pm 0.002$  absorbance units.

$$\lambda = 390\text{nm}$$

Abs.	R	log R
.382	0	$-\infty$
.398	0.00020	-3.699
.452	0.00100	-3.000
.515	0.00200	-2.699
.600	0.00400	-2.398
.400	0.0200	-1.699

$$\lambda = 395\text{nm}$$

Abs.	R	log R
.372	0	$-\infty$
.395	0.00020	-3.699
.461	0.00100	-3.000
.540	0.00200	-2.699
.655	0.00400	-2.398
.492	0.0200	-1.699



$\lambda = 400\text{nm}$

Abs	R	log R
.361	0	$-\infty$
.387	0.00020	-3.699
.463	0.00100	-3.000
.558	0.00200	-2.699
.700	0.00400	-2.398
.600	0.0200	-1.699

$\lambda = 405\text{nm}$

Abs	R	log R
.345	0	$-\infty$
.373	0.00020	-3.699
.460	0.00100	-3.000
.564	0.00200	-2.699
.729	0.00400	-2.398
.694	0.0200	-1.699

$\lambda = 410\text{nm}$

Abs	R	log R
.326	0	$-\infty$
.357	0.00020	-3.699
.447	0.00100	-3.000
.560	0.00200	-2.699
.739	0.00400	-2.398
.804	0.0200	-1.699

$\lambda = 415\text{nm}$

Abs	R	log R
.305	0	$-\infty$
.336	0.00020	-3.699
.430	0.00100	-3.000
.543	0.00200	-2.699
.738	0.00400	-2.398
.885	0.0200	-1.699





$\lambda = 420 \text{ nm}$

Abs	R	log R
.284	0	$-\infty$
.315	0.00020	-3.699
.403	0.00100	-3.000
.520	0.00200	-2.699
.717	0.00400	-2.398
.954	0.0200	-1.699

$\lambda = 425 \text{ nm}$

Abs	R	log R
.256	0	$-\infty$
.289	0.00020	-3.699
.375	0.00100	-3.000
.485	0.00200	-2.699
.682	0.00400	-2.398
.998	0.0200	-1.699

$\lambda = 430 \text{ nm}$

Abs	R	log R
.235	0	$-\infty$
.262	0.00020	-3.699
.342	0.00100	-3.000
.448	0.00200	-2.699
.636	0.00400	-2.398
1.018	0.0200	-1.699

$\lambda = 435 \text{ nm}$

Abs	R	log R
.209	0	$-\infty$
.235	0.00020	-3.699
.310	0.00100	-3.000
.401	0.00200	-2.699
.584	0.00400	-2.398
1.010	0.0200	-1.699

$\lambda = 440 \text{ nm}$

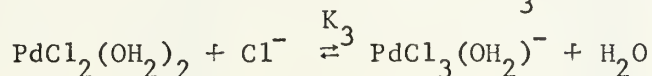
Abs	R	log R
.182	0	$-\infty$
.208	0.00020	-3.699
.265	0.00100	-3.000
.362	0.00200	-2.699
.530	0.00400	-2.398
.978	0.0200	-1.699



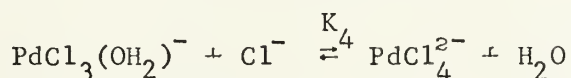
## APPENDIX C

### ABSORBANCE DATA FOR DETERMINING $K_3$ AND $K_4$

The absorbance data in this appendix came from the spectra of Fig (2) and was used to determine values for  $K_3$  for the equilibrium:



Additionally, the data was fitted to the normalized curves of Fig. (3) to yield values of  $K_4$  for the reaction:



As in appendix B, the absorbance is accurate to  $\pm 0.002$  absorbance units and the ligand ratio to three significant figures. Log R is accurate to three decimal places.

$\lambda = 420 \text{ nm}$

Abs.	R	log R
.240	0.997	-0.001
.257	1.69	0.227
.271	2.48	0.395
.283	3.30	0.519
.368	9.71	0.987
.415	15.9	1.201
.480	30.3	1.481
.587	76.9	1.886
.662	333	2.523

$\lambda = 425 \text{ nm}$

Abs.	R	log R
.270	0.997	-0.001
.285	1.69	0.227
.300	2.48	0.395
.310	3.30	0.519
.400	9.71	0.987
.450	15.9	1.201
.513	30.3	1.481
.618	76.9	1.886
.686	333	2.523



$\lambda = 430 \text{ nm}$

Abs.	R	log R
.298	0.997	-0.001
.314	1.69	0.227
.329	2.48	0.395
.341	3.30	0.519
.427	9.71	0.987
.474	15.9	1.201
.538	30.3	1.481
.637	76.9	1.886
.690	333	2.523

$\lambda = 435 \text{ nm}$

Abs	R	log R
.332	0.997	-0.001
.343	1.69	0.227
.357	2.48	0.395
.369	3.30	0.519
.448	9.71	0.987
.494	15.9	1.201
.552	30.3	1.481
.639	76.9	1.886
.682	333	2.523

$\lambda = 440 \text{ nm}$

Abs	R	log R
.358	0.997	-0.001
.373	1.69	0.227
.385	2.48	0.395
.396	3.30	0.519
.467	9.71	0.987
.506	15.9	1.201
.557	30.3	1.481
.631	76.9	1.886
.658	333	2.523

$\lambda = 445 \text{ nm}$

Abs	R	log R
.390	0.997	-0.001
.404	1.69	0.227
.414	2.48	0.395
.420	3.30	0.519
.482	9.71	0.987
.514	15.9	1.201
.555	30.3	1.481
.611	76.9	1.886
.625	333	2.523



$\lambda = 450 \text{ nm}$

Abs	R	log R
.422	0.997	-0.001
.433	1.69	0.227
.440	2.48	0.395
.447	3.30	0.519
.493	9.71	0.987
.519	15.9	1.201
.548	30.3	1.481
.586	76.9	1.886
.590	333	2.523

$\lambda = 455 \text{ nm}$

Abs	R	log R
.451	0.997	-0.001
.462	1.69	0.227
.466	2.48	0.395
.471	3.30	0.519
.503	9.71	0.987
.522	15.9	1.201
.536	30.3	1.481
.560	76.9	1.886
.545	333	2.523

$\lambda = 460 \text{ nm}$

Abs	R	log R
.479	0.997	-0.001
.486	1.69	0.227
.488	2.48	0.395
.490	3.30	0.519
.509	9.71	0.987
.519	15.9	1.201
.521	30.3	1.481
.530	76.9	1.886
.507	333	2.523

$\lambda = 470 \text{ nm}$

Abs	R	log R
.515	0.997	-0.001
.518	1.69	0.227
.517	2.48	0.395
.515	3.30	0.519
.513	9.71	0.987
.506	15.9	1.201
.487	30.3	1.481
.469	76.9	1.886
.430	333	2.523





$\lambda = 475 \text{ nm}$

Abs	R	log R
.521	0.997	-0.001
.521	1.69	0.227
.520	2.48	0.395
.517	3.30	0.519
.506	9.71	0.987
.494	15.9	1.201
.465	30.3	1.481
.441	76.9	1.886
.396	333	2.523

$\lambda = 480 \text{ nm}$

Abs	R	log R
.517	0.997	-0.001
.518	1.69	0.227
.516	2.48	0.395
.510	3.30	0.519
.493	9.71	0.987
.477	15.9	1.201
.442	30.3	1.481
.410	76.9	1.886
.361	333	2.523



## APPENDIX D

### ABSORBANCES AND FORMATION CONSTANTS

The data in this appendix are absorbances and overall formation constants determined as a function of wavelength. These data were then used in the calculation of the values reported in this thesis for the four stepwise formation constants of the system going from  $\text{Pd}(\text{OH}_2)_4^{2+}$  to  $\text{PdCl}_4^{2-}$ .

#### Data for Determining $\log K_1$

$\lambda$ (nm)	$A_1$	$\log \beta_1$
390	1.191	1.960
395	1.580	1.881
400	1.758	1.920
405	1.840	1.905
410	1.928	1.900
415	2.004	1.890
420	2.074	1.884
425	2.048	1.900
430	2.027	1.852
435	1.910	1.835
440	1.774	1.830

#### Data for Determining $\log K_2$

$\lambda$ (nm)	$A_2$	$\log \beta_1$	$\log \beta_2$
390	0	2.041	4.009
395	0	1.974	4.000
400	0	1.960	3.896
405	0	1.971	3.813
410	0	1.973	3.705
415	0	1.950	3.600
420	0.077	1.908	3.517
425	0	1.904	3.386
430	0.046	1.851	3.237
435	0.005	1.846	3.097
440	0	1.856	3.062



Data for Determining  $\log K_3$

$\lambda$ (nm)	$A'_2$	$\log \beta'_1$	$\log \beta'_2$
420	0	1.466	5.312
425	0	1.451	5.238
430	0.026	1.470	4.996
435	0.040	1.351	5.384
440	0.061	1.455	4.870
445	0.080	1.280	5.083
450	0.100	1.263	4.987
455	0.530	1.510	3.225
460	0.485	1.415	3.432
475	0.378	1.714	3.841

Data for Determining  $\log K_4$

$\lambda$ (nm)	$A'_1$	$\log \beta'_2$
420	0.730	1.450
425	0.758	1.400
430	0.790	1.450
435	0.725	1.400
440	0.760	1.500
445	0.667	1.320
450	0.630	1.380
455	0.650	1.510
460	0.580	1.440
470	0.425	1.560
475	0.420	1.380
480	0.335	1.500



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## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

ORIGINATING ACTIVITY (Corporate author)

Naval Postgraduate School  
Monterey, California 93940

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

REPORT TITLE

Stability Constants for the Chloride Complexes of Palladium (II)

DESCRIPTIVE NOTES (Type of report and, inclusive dates)

Master's Thesis; December 1972

AUTHOR(S) (First name, middle initial, last name)

Richard Leon Burke

REPORT DATE

December 1972

7a. TOTAL NO. OF PAGES

62

7b. NO. OF REFS

22

CONTRACT OR GRANT NO.

9a. ORIGINATOR'S REPORT NUMBER(S)

PROJECT NO.

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

DISTRIBUTION STATEMENT

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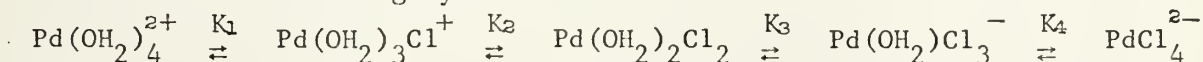
SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

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ABSTRACT

Using absorbance data from Pd (II) solutions containing varying amounts of chloride ion, the stepwise formation constants were determined for the following system:



The values for  $K_1$  and  $K_4$  were obtained by curve fitting methods.  $K_2$  and  $K_3$  were found by regression and required statistical adjustment.

Anomalies arising from the resulting values and values obtained by other workers were discussed. Suggestions for further work in the chloro- Pd(II) system were made.



KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Stability Constants						
Tetrachloropalladium (II)						
Tetraaquopalladium (II)						





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